Title: ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC COMPOUNDS: CRYSTAL STRUCTURE OF [Et₂Al₂As(SiMe₃)₂]₂

Personal Author(s): Wells, A.T. McPhail, and T. M. Speer

Type of Report: Technical

Date of Report: 1991-10-03

Page Count: 18

Abstract: Accepted for publication in Organometallics.

Subject Terms: aluminum-arsenic, synthesis, crystal structure, ring compound

Abstract: See attached.
On the Synthesis and Characterization of Novel Aluminum-Arsenic Compounds; Crystal Structure of \([\text{Et}_2\text{AlAs(SiMe}_3\text{)}_2]\)2.

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

Department of Chemistry, Paul M. Gross Chemical Laboratory
Duke University, Durham NC, 27706
(Received ......, 1991)

ABSTRACT

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type \(\text{Al-As-Al-As}\) and \(\text{Al-As-Al-Cl}\) was investigated. The second fully characterized aluminum-ar senic dimer, \([\text{Et}_2\text{AlAs(SiMe}_3\text{)}_2]\)2 (1), was isolated from a coupling reaction between \(\text{Et}_2\text{AlCl}\) and \(\text{LiAs(SiMe}_3\text{)}_3\) carried out at -78 °C. Dehalosilylation reactions between \(\text{Et}_2\text{AlCl}\) and \(\text{As(SiMe}_3\text{)}_3\) in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected products, instead yielding the adduct \(\text{Et}_2\text{(Cl)Al-As(SiMe}_3\text{)}_3\) (2). As evidenced by \(^1\text{H NMR spectra, an NMR tube sample of } 2\text{ in benzene-d}_6\text{ did undergo internal dehalosilylation to give 1 when heated to 87 °C in an oil bath. X-ray crystallographic analysis of 1 confirms its dimeric solid-state structure and shows the } \text{Al-As-Al-As} \text{ ring to be planar. Compound 1 crystallizes in the monoclinic system, space group } C2/c (C2\text{h})^6, \text{ with four molecules in a unit cell of dimensions: } a = 18.214(2) \text{ Å, } b = 9.542(1) \text{ Å, } c = 20.453(2) \text{ Å, } \beta = 99.89(1)^\circ.\)
ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC COMPOUNDS: CRYSTAL STRUCTURE OF \([\text{Et}_2\text{AlAs(SiMe}_3)_2]\)_2

by

R. L. Wells, A. T. McPhail, and T. M. Speer

Prepared for Publication in *Organometallics*

Duke University
Department of Chemistry
Durham, NC 27706

October 3, 1991

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited
On the Synthesis and Characterization of Novel Aluminum-Arsenic Compounds; Crystal Structure of \([\text{Et}_2\text{AlAs(SiMe}_3\text{)}_2\text{]}_2\).

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

Department of Chemistry, Paul M. Gross Chemical Laboratory
Duke University, Durham NC, 27706
(Received ......, 1991)

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type \(\text{Al-As-Al-As}\) and \(\text{Al-As-Al-Cl}\) was investigated. The second fully characterized aluminum-arsenic dimer \([\text{Et}_2\text{AlAs(SiMe}_3\text{)}_2\text{]}_2\) (1), was isolated from a coupling reaction between \(\text{Et}_2\text{AlCl}\) and \(\text{LiAs(SiMe}_3\text{)}_3\) carried out at -78 °C. Reactions between \(\text{Et}_2\text{AlCl}\) and \(\text{As(SiMe}_3\text{)}_3\) in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected dehalosilylation products, instead yielding the adduct \(\text{Et}_2(\text{Cl})\text{Al\cdotAs(SiMe}_3\text{)}_3\) (2). As evidenced by \(^1\text{H NMR spectra, an NMR tube sample of 2 in benzene-}\text{d}_6\text{ did undergo internal dehalosilylation to give 1 when heated to 87 °C in an oil bath. X-ray crystallographic analysis of 1 confirms its dimeric solid-state structure and shows the }\text{Al-As-Al-As}\text{ ring to be planar. Compound 1 crystallizes in the monoclinic system, space group }C2/c (C\text{2h}_6),\text{ with four molecules in a unit}
INTRODUCTION

Of late, there has been heightened interest in the preparation of compounds that may serve as single-source precursors to Group 13-15 semiconductor materials.\textsuperscript{1,2} Two methods have been developed in our laboratories to fabricate compounds that may prove useful to this end: a) dehalosilylation between tris(trimethylsilyl)arsine and a Group 13 halide and b) coupling reactions involving lithium bis(trimethylsilyl)arsenide and a Group 13 halide. These methodologies have been applied to systems involving the heavier Group 13 elements to prepare compounds with core rings of the type $\text{M-As-M-As}$ and $\text{M-As-M-Cl}$, where $\text{M = Ga}$ and $\text{In}$.\textsuperscript{3-7} In an attempt to utilize these tactics to prepare analogous aluminum-arsenic species, reaction of $\text{Et}_2\text{AlCl}$ with tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide was undertaken. While proving useful in the cases of Ga and In, room temperature dehalosilylation reactions failed in this work instead yielding the adduct $\text{Et}_2(\text{Cl})\text{Al\textbullet As(SiMe}_3)_3$ (2). The novel dimer $[\text{Et}_2\text{AlAs(SiMe}_3)_2]_2$ (1), was prepared by a coupling reaction and is only the second Al-As dimer fully characterized by single crystal X-ray analysis.

EXPERIMENTAL

General Considerations. All reactions and manipulations were carried out utilizing standard Schlenk techniques, under an Ar atmosphere in a Vacuum/Atmospheres HE-43 Dri-Lab or under vacuum. Pentane and hexane were dried over LiAlH\textsubscript{4} while all other solvents were dried over, and distilled from, sodium benzophenone ketyl. Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide
were prepared by the methods of Becker et al. Diethylaluminum chloride was purchased from Strem Chemicals, Inc. and used without further purification. $^1$H, $^{13}$C{$^1$H} and $^{27}$Al{$^1$H} NMR spectra were obtained at 299.943, 75.4 and 78.2 MHz, respectively, on a Varian XL-300 spectrometer in 5 mm tubes. $^{13}$C{$^1$H} and $^1$H NMR spectra were referenced to TMS using the carbons or residual protons of benzene-$d_6$ at $\delta$ 128 ppm and $\delta$ 7.15 ppm, respectively. $^{27}$Al{$^1$H} spectra were referenced externally to Al(NO$_3$)$_3$ at $\delta$ 0.00 ppm. All spectra were run in benzene-$d_6$ and NMR tubes were flame sealed under vacuum. Melting points were obtained on a Hoover Uni-Melt in sealed capillaries and are uncorrected. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Crystals used in X-ray analyses were flame sealed under argon in 0.7 mm thin-walled glass capillaries. Volatile reaction products were analyzed for Me$_3$SiCl content by hydrolysis with deionized water followed by titration of the resulting HCl solution with standard NaOH to a phenolphthalein endpoint. NaOH was standardized against potassium hydrogen phthalate to a phenolphthalein endpoint.

Preparation of [Et$_2$AlAs(SiMe$_3$)$_2$]$_2$ (1). LiAs(SiMe$_3$)$_2$ (0.373 g, 1.63 mmol) was dissolved in 25 mL of pentane and 10 mL of THF in the top bulb of a two-bulb reaction flask. Et$_2$AlCl (0.1969 g, 1.633 mmol) was washed into the bottom bulb with 35 mL pentane. The lower bulb was cooled to -78 °C in an acetone/dry ice bath and the upper bulb was cooled with a liquid nitrogen wand. Upon mixing, a white precipitate formed (presumably LiCl, 0.0588 g, 87% yield) and the solution remained clear. After stirring for 18 h at -78 °C, the reaction mixture was allowed to warm slowly to room temperature and volatiles were removed in vacuo to leave an off-white semi-solid that was recrystallized at -15 °C from pentane to give 1 (0.651 g, 65.2% yield), mp 201 °C. No Me$_3$SiCl was eliminated over the course of the reaction. Anal. Calcd. (found) for C$_{20}$H$_{56}$Al$_2$As$_2$Si$_4$: C 39.20 (39.40), H 9.15 (9.16). $^1$H NMR: $\delta$ 0.42
Preparation of $\text{Et}_2(\text{Cl})\text{Al}
\cdot \text{As(SiMe}_3\text{)}_3$ (2). (a) Reaction of $\text{Et}_2\text{AlCl}$ with $\text{As(SiMe}_3\text{)}_3$ (1:1 mole ratio). $\text{Et}_2\text{AlCl}$ (0.2058 g, 1.670 mmol) in 25 mL of pentane was added to $\text{As(SiMe}_3\text{)}_3$ (0.492 g, 1.67 mmol) in 25 mL of pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was noted upon mixing. Following stirring at room temperature for 3 d, volatiles were removed in vacuo leaving an off-white solid that was recrystallized from pentane at -15 °C to give 2 (0.684 g, 98.7% yield), mp 138 °C. No $\text{Me}_3\text{SiCl}$ was eliminated over the course of the reaction. Anal. Calcd. (Found) for $\text{C}_{13}\text{H}_{37}\text{AlAsClSi}_3$: C 37.62 (37.37), H 8.99 (8.89), Cl 8.54 (8.12). $^1\text{H NMR}$: $\delta$ 0.28 [s, Si(CH$_3$)$_3$, 27 H], 0.46 (q, CH$_2$, 4H), 1.52 (t, CH$_3$, 6H). $^{13}\text{C}{^1\text{H}}$ NMR: $\delta$ 3.09 (s, Si(CH$_3$)$_3$), 9.77 (s, CH$_3$), CH$_2$ not observed. $^{27}\text{Al}{^1\text{H}}$ NMR: $\delta$ 165.32 (br s). (b) Reaction of $\text{Et}_2\text{AlCl}$ with $\text{As(SiMe}_3\text{)}_3$ (2:1 mole ratio). $\text{Et}_2\text{AlCl}$ (0.3934 g, 3.20 mmol) in 20 mL pentane was added to $\text{As(SiMe}_3\text{)}_3$ (0.470 g, 1.60 mmol) in 30 mL pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was seen upon addition. Following stirring for 3 d at room temperature, volatiles were removed in vacuo to leave an off-white solid which was recrystallized from pentane at -15 °C to give clear crystals (0.653 g 98.3% yield), mp and NMR spectra ($^1\text{H}$ and $^{13}\text{C}{^1\text{H}}$) match those of an authentic sample of 2, vide supra. No $\text{Me}_3\text{SiCl}$ was eliminated over the course of the reaction.

Intramolecular Dehalosilylation of 2 to Form 1. An NMR tube sample of 2 in benzene-d$_6$ was heated to 87 °C in an oil bath for 4 d. $^1\text{H NMR}$ spectra taken over this time showed peaks consistent with an authentic sample of 1 and one that may be attributed to $\text{Me}_3\text{SiCl}$ at $\delta$ 0.165, indicating that internal dehalosilylation occurred.
Attempted Conversion of 1 to \( \text{Et}_2\text{AlAs(SiMe}_3\text{)}_2\text{Al(Et)}_2\text{Cl} \). \( \text{Et}_2\text{AlCl} \) (0.0376 g, 0.312 mmol) in 20 mL of pentane was added to 1 (0.0956 g, 0.156 mmol) in a one-necked, round-bottomed flask fitted with a Teflon valve and equipped with a magnetic stir bar. Following stirring for 2 d at room temperature, volatiles were removed \textit{in vacuo} to leave an off white semi-solid that was recrystallized from pentane at -15 °C, mp and NMR spectra (\( \text{Its} \text{ } ^1\text{H} \) and \( ^{13}\text{C}\{^1\text{H}\} \)) matched those of an authentic sample of 1, \textit{vide supra}, indicating no reaction had occurred.

**X-Ray Crystal Structure Analysis of 1.** Crystallographic data are summarized in Table I. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the \( \phi \)-dependency of the intensities of several reflections with \( \psi \) ca. 90°, was also applied. The crystal structure was solved by the heavy-atom approach. The systematically absent reflections: \( hkl \) when \( h + k \neq 2n \) and \( h0l \) when \( l \neq 2n \), are compatible with two space groups, viz. \( Cc \) and \( C2/c \). With only four formula units in the latter, dimeric molecules must either lie on a crystallographic center of symmetry or \( C_2 \) symmetry axis. Approximate coordinates for the As atoms, derived from a Patterson map, were related by a center of symmetry and thus all further calculations were performed using equivalent positions appropriate to the centrosymmetric space group \( C2/c \). The remaining non-hydrogen atoms were located in a series of weighted \( F_0 \) and difference Fourier syntheses. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) and an extinction correction was included as a variable. A final difference Fourier synthesis contained no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 9.
DISCUSSION

Dehalosilylation reactions between a Group 13 halide and As(SiMe₃)₃ have been used to prepare dimeric and mixed bridge species, M-As-M-As and M-As-M-Cl, respectively, where M = Ga and In. It has been shown that in the case of indium halides, dimers may be prepared if reaction is carried out in a 1:1 mole ratio and mixed bridges if a 2:1 stoichiometry of In to As reagents is employed. However, no gallium-arsenic dimers have been isolated utilizing such reactions. Instead, only mixed bridge products have been obtained in reactions of either 1:1 or 2:1 stoichiometry of Ga to As reactants. While this method has been shown to be of general utility in these systems, seminal investigations show it to fail as group three is ascended to aluminum. Thus, reaction of Et₂AlCl with As(SiMe₃)₃ at ambient temperature in either 1:1 or 2:1 stoichiometry (eq 1) gives only 2 with no evidence of silyl cleavage.

\[
n\text{Et}_2\text{AlCl} + \text{As(SiMe}_3\text{)}_3 \rightarrow \text{Et}_2\text{(Cl)Al•As(SiMe}_3\text{)}_3 + (n-1)\text{Et}_2\text{AlCl} \quad (1)
\]

This behavior may be understood by consideration of the relative strengths of the Group 13-Cl bonds. They are 420.7, 354.0 and 328.0 kJmol⁻¹ for Al, Ga and In, respectively. Since this bond is much stronger in the case of aluminum, its cleavage may be energetically unfavored and, hence, dehalosilylation is not observed. Instead, simple adducts are formed. To date, reaction conditions have not been varied to elucidate the effect of temperature upon such reactions. Such steps may provide a driving force that would enable dehalosilylation to occur.

While crystals of 2 suitable for single crystal X-ray analysis have not been obtained, other data support the postulation of its structure as an adduct. Its ^1H,
$^{13}\text{C}\{^1\text{H}\}$ and $^{27}\text{Al}\{^1\text{H}\}$ NMR spectra suggest such a formulation in that the $^1\text{H}$ integration and splitting patterns are compliant, the $^{13}\text{C}\{^1\text{H}\}$ spectrum intensities are appropriate for those peaks observed and only one type of aluminum is present as evidenced by a single peak in the $^{27}\text{Al}\{^1\text{H}\}$ spectrum. This, coupled with a partial elemental analysis (C, H and Cl), the fact that no Me$_3$SiCl was found in reaction volatiles and that yield was nearly quantitative, indicates that the structure of the product is correctly stated as 2.

It was previously shown by us that the adduct Cl$_3$Al·As(SiMe$_3$)$_3$ undergoes intramolecular dehalosilylation to give AlAs when heated neat, under vacuum, in a cool flame. With this in mind, attempted internal dehalosilylation of 2 was undertaken. Here, however, it was achieved at a much lower temperature. An NMR tube sample of 2 in benzene-d$_6$ was heated at 87 °C for four days. $^1\text{H}$ NMR spectra taken as early as one day after heating showed peaks that may be attributed to compound 1 and Me$_3$SiCl. Thus, dehalosilylation may be brought about under very mild conditions in the case of 2 (eq 2).

$$2\text{Et}_2(\text{Cl})\text{Al·As(SiMe}_3)_3 \rightarrow [\text{Et}_2\text{AlAs(SiMe}_3)_2]_2 + 2\text{Me}_3\text{SiCl}$$

(2)

Compound 1 was prepared initially in relatively high yield (65%) by employing a coupling reaction between LiAs(SiMe$_3$)$_2$ and Et$_2$AlCl at -78 °C (eq 3). When carried out at room temperature, product was obtained in very low yield with an uncharacterized viscous, orange liquid as the predominant product. It is noteworthy
that, prior to this work, only four other arsinoalanes had ever been reported.\textsuperscript{12-15} Three of them are dimers\textsuperscript{12,14,15}, but only one was fully characterized by single crystal X-ray analysis\textsuperscript{16}

The conversion of sundry Group 13-As dimers to mixed-bridge compounds by treatment with two mole equivalents of a dialkyl Group 13 halide has been shown to be applicable to such Ga and In containing species.\textsuperscript{5,16,17} However, it was found that this methodology was not successful for 1. Upon treatment with two mole equivalents of Et\textsubscript{2}AlCl, no reaction was observed (eq 4), as evidenced by \textsuperscript{1}H and \textsuperscript{13}C NMR spectra.

\[
\text{[Et}_2\text{AlAs(SiMe}_3)_2\text{]}_2 + 2\text{Et}_2\text{AlCl} \quad \xrightarrow{\text{\textrightarrow}} \quad 2\text{Et}_2\text{AlAs(SiMe}_3)_2\text{Al(Et)}_2\text{Cl}
\]

(4)

This suggests that perhaps the dimer does not undergo dissociation in solution, thus not allowing for the monomeric unit to react with the aluminum halide.

Crystals of 1 suitable for X-ray analysis were grown from pentane. Crystallographic data are reported in Table I. An ORTEP diagram showing the atom numbering scheme is presented in Figure I. Table II lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters while selected bond lengths and angles are given in Table III.

Compound 1 crystallizes in the monoclinic space group \textit{C2/c} with the four discrete dimeric molecules in the unit cell lying on crystallographic centers of symmetry, and thus the \textsuperscript{Al-As-Al-As\textsuperscript{-}} ring is constrained to be exactly planar as is the case for the only other previously characterized aluminum-ar senic dimer, [Et\textsubscript{2}AlAs(t-Bu)\textsubscript{2}]\textsubscript{2} (3).\textsuperscript{15} The mean Al-As distance of 2.535 Å in 1 is slightly shorter that that of 2.567 Å in 3. The mean of the Al-C(1) [1.965(6) Å] and Al-C(3) [1.986(6) Å] bond distances at 1.976 Å in 1 is also slightly less than the corresponding mean of 1.992 Å in 3. The geometry
about the Al and As atoms in 1 is distorted tetrahedral with the endocyclic angle subtended at As [Al-As-Al' = 91.01(5)°] being slightly larger than that at Al [As-Al-As' = 88.99(5)°]; the difference between the Al-As-Al' and As-Al-As' angles in 3 [94.54(4)° vs. 85.64(4)°] is much more pronounced. The Si-As-Si and C-Al-C angles at 107.59(6)° and 115.0(3)° in 1 deviate from tetrahedral in the same sense as do the C-As-C and C-Al-C angles, 108.9(3)° and 111.5(3)°, respectively, in 3.

Compound 1 is of particular interest because it may be useful as a single-source precursor for the facile formation of AlAs. There are several ways in which this molecule may be envisaged as being utilized for such purposes. The ethyl groups provide for the possibility of β-hydrogen transfer with concurrent evolution of ethene and subsequent elimination of trimethylsilane to give AlAs. A second possibility is alcoholysis. Douglas and Theopold showed that a Ga-As dimer, when treated with methanol, underwent internal elimination to give GaAs. The third way in which AlAs might be obtained is to take advantage of the fact that covalent halides are known to cleave the silicon-arsenic bond. Thus, treatment of 1 with HCl should afford Me₃SiCl and an AsH₂-containing species which should readily eliminate ethane, or ethene and dihydrogen, to yield AlAs.

CONCLUSIONS

The work presented herein shows the viability of lithium chloride elimination reactions in the preparation of aluminum-arsenic dimers. While this methodology was successfully applied, dehalosilylation reactions were ineffective in that an aluminum-arsenic-chlorine mixed-bridge compound nor a dimer could be prepared directly by this route; albeit, evidence was obtained which indicated an adduct underwent dehalosilylation on heating to give a dimer. This study will be used as a starting point for further investigation of aluminum-arsenic systems. Through variation of temperature, substituents on aluminum and other reaction conditions a better
understanding of the limitations and applications of lithium halide elimination and
dehalosilylation reactions to the preparation of single-source precursors to AlAs may
be developed.

Acknowledgements. Financial support from the Office of Naval Research is
greatly appreciated.

Supplementary Materials Available: Tables of hydrogen atom
coordinates and isotropic thermal parameters, anisotropic temperature factors,
complete lists of interatomic distances and angles, including torsion angles for 1, and
equations of least-squares planes through groups of atoms (5 pages); a listing of
observed and calculated structure amplitudes for 1 (14 pages). Ordering information
is given on any current masthead page.
References


Caption to Figure

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the solid-state conformation and atom numbering scheme of \([\text{Et}_2\text{AlAs(SiMe}_3\text{)}_2]_2\) (1); primed atoms are related to unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1. Crystallographic Data(^a) for [Et(_2)AlAs(SiMe(_3))(_2)](_2) (1)</td>
<td></td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C(<em>{20})H(</em>{65})Al(_2)As(_2)Si(_4)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>612.82</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C(_2)/(\sigma(C(_2)h(_6))) - No.15</td>
</tr>
<tr>
<td>a(Å)</td>
<td>18.214(2)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>9.542(1)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>20.453(2)</td>
</tr>
<tr>
<td>(\beta(°))</td>
<td>99.89(1)</td>
</tr>
<tr>
<td>No. of orientation refls.; (\theta(°)) range</td>
<td>25; 40-45</td>
</tr>
<tr>
<td>(V(Å^3))</td>
<td>3502(1)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(D_{\text{calc.}}) (g cm(^{-3}))</td>
<td>1.162</td>
</tr>
<tr>
<td>(\mu) (Cu-K(\alpha) radiation, l = 1.5418 Å)</td>
<td>42.5</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>23</td>
</tr>
<tr>
<td>Crystal dimensions (mm)</td>
<td>0.15 x 0.25 x 0.32</td>
</tr>
<tr>
<td>(T_{\text{max}}:T_{\text{min}})</td>
<td>1.00:0.65</td>
</tr>
<tr>
<td>Scan type</td>
<td>(\omega)-(2\theta)</td>
</tr>
<tr>
<td>Scanwidth (°)</td>
<td>0.70 + 0.14\tan(\theta)</td>
</tr>
<tr>
<td>(\theta_{\text{max}}) (°)</td>
<td>75</td>
</tr>
<tr>
<td>Intensity control refls.; (h) variation; repeat time (hr)</td>
<td>3 1 2, 2 2 2, 1 3 (\overline{1}), 2 2 (\overline{4}); (&lt;2%); 2</td>
</tr>
<tr>
<td>Total no. of refls. (+(h),+k,±l) recorded</td>
<td>3705</td>
</tr>
<tr>
<td>No. of non-eqiv. refls. recorded</td>
<td>3118</td>
</tr>
<tr>
<td>(R_{\text{merge}}) (on (l))</td>
<td>0.023</td>
</tr>
<tr>
<td>No. of refls. retained ([l &gt; 3.0\sigma(l)])</td>
<td>1968</td>
</tr>
<tr>
<td>No. of parameters refined</td>
<td>128</td>
</tr>
<tr>
<td>Extinction correction</td>
<td>3.7(1) \times 10(^{-6})</td>
</tr>
<tr>
<td>(R(R_w))</td>
<td>0.039 (0.053)</td>
</tr>
<tr>
<td>Goodness-of-fit(^c)</td>
<td>1.11</td>
</tr>
<tr>
<td>Max. shift:esd in final least-squares cycle</td>
<td>0.02</td>
</tr>
<tr>
<td>Final (\Delta\rho(\text{e/Å}^3)) max.;min.</td>
<td>0.32; -0.58</td>
</tr>
</tbody>
</table>

\(^a\)An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/4
Table 1. (Continued)

and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP).

\[ bR = \sum |F_o| - |F_c|/\Sigma |F_o|; \quad R_w = \left[ \Sigma \omega (|F_o| - |F_c|)^2/\Sigma \omega |F_o|^2 \right]^{1/2}; \quad \Sigma \omega \Delta^2 \left[ \omega = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|) \right] \text{ was minimized.} \]

\[ \text{CGoodness-of-fit} = \left[ \Sigma \omega \Delta^2/(N_{\text{observations}} - N_{\text{parameters}}) \right]^{1/2}. \]
Table II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}(\text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.18753(3)</td>
<td>0.25453(6)</td>
<td>-0.07961(2)</td>
<td>4.06(1)</td>
</tr>
<tr>
<td>Al</td>
<td>0.18075(7)</td>
<td>0.3337(2)</td>
<td>0.04040(7)</td>
<td>4.25(3)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>0.10419(8)</td>
<td>0.0731(2)</td>
<td>-0.11613(7)</td>
<td>5.27(3)</td>
</tr>
<tr>
<td>Si(2)</td>
<td>0.17122(9)</td>
<td>0.4338(2)</td>
<td>-0.15669(7)</td>
<td>5.68(3)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.1045(3)</td>
<td>0.2321(6)</td>
<td>0.0788(3)</td>
<td>5.7(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.1042(4)</td>
<td>0.2663(7)</td>
<td>0.1520(3)</td>
<td>7.5(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.1774(3)</td>
<td>0.5409(6)</td>
<td>0.0486(3)</td>
<td>6.7(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.1042(4)</td>
<td>0.6022(8)</td>
<td>0.0471(5)</td>
<td>11.8(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>0.1094(4)</td>
<td>-0.0631(7)</td>
<td>-0.0520(3)</td>
<td>7.8(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.0072(3)</td>
<td>0.1409(8)</td>
<td>-0.1347(4)</td>
<td>9.4(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.1301(4)</td>
<td>-0.0092(8)</td>
<td>-0.1915(3)</td>
<td>8.2(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>0.0790(4)</td>
<td>0.5213(9)</td>
<td>-0.1594(4)</td>
<td>10.0(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>0.1754(4)</td>
<td>0.3628(9)</td>
<td>-0.2401(3)</td>
<td>8.3(2)</td>
</tr>
<tr>
<td>C(23)</td>
<td>0.2467(4)</td>
<td>0.5662(7)</td>
<td>-0.1334(4)</td>
<td>8.8(2)</td>
</tr>
</tbody>
</table>
Table III. Selected Bond Distances (Å) and Angles (deg) for 1 with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th></th>
<th>Bond Angles</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Al</td>
<td>2.539(2)</td>
<td>Al-As-Si(1)</td>
<td>114.10(6)</td>
</tr>
<tr>
<td>As-Si(2)</td>
<td>2.347(2)</td>
<td>Al-As-Si(2)</td>
<td>114.79(6)</td>
</tr>
<tr>
<td>Al-C(1)</td>
<td>1.965(6)</td>
<td>Si(1)-As-Si(2)</td>
<td>107.59(6)</td>
</tr>
<tr>
<td>As-AI'</td>
<td>2.531(1)</td>
<td>Si(2)-As-AI'</td>
<td>116.60(6)</td>
</tr>
<tr>
<td>As-Al-C(1)</td>
<td></td>
<td>As-Al-C(3)</td>
<td>112.5(2)</td>
</tr>
<tr>
<td>As-Al-As'</td>
<td></td>
<td>C(1)-Al-C(3)</td>
<td>115.0(3)</td>
</tr>
<tr>
<td>Ci(i)-Al-As'</td>
<td></td>
<td>C(3)-Al-As'</td>
<td>110.3(2)</td>
</tr>
</tbody>
</table>
TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, VA 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, IN 47522-5050

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, DC 20375-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering Lab.
Code L52
Port Hueneme, CA 93043

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Dr. Eugene C. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

Chief of Naval Research (1)
Special Assistant for Marine Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314